Longleaf Pine: Seeing the Forest through the Trees

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Old Resinous Turpentine Stumps as an Indicator of the Range of Longleaf Pine in Southeastern Virginia

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Abstract

Wood anatomy cannot be used to differentiate between the southern yellow pine species. Wood samples collected from old resinous turpentine stumps in coastal Virginia were subjected to chemical and spectroscopic analyses in an effort to determine if they could be identified as longleaf pine. The age and resinous nature of the samples were manifested in high specific gravities, the presence of oxidized monoterpenes, and the ability to be grouped separately from wood from recently harvested trees by NIR spectroscopy. Since there are no standards for old resinous pine stumps, studies are continuing to determine changes that occur in longleaf pine stumps aged under field conditions.

Introduction

Longleaf pine (*Pinus palustris* Mill.) is the third most abundant pine species in the southeastern United States (Koch 1972). Straight growth, coupled with wood that is strong and hard, made this pine species highly desirable for poles, construction lumber, and flooring. Longleaf pine also has a well established history in naval stores production, from early turpentining operations to the subsequent processing of residual stumps, especially those from trees harvested in the late 19th and early 20th centuries (Gardner 1989). The range for longleaf pine spans from southeastern Virginia to eastern Texas (Koch 1972). In Virginia, harvesting practices and changes in land use since colonial settlement has dramatically reduced the presence of longleaf pine. Of the original 1.5 million acres of longleaf forest estimated to exist prior to colonial settlement, only 800 acres remain (Sheridan et al. 1999). Longleaf pine restoration efforts have initiated studies to verify its range by determining the species of very old turpentine stumps. Our efforts were directed towards determining if chemical and physical characterizations of wood taken from selected stumps could provide information indicating the likely pine species.

Materials and Methods

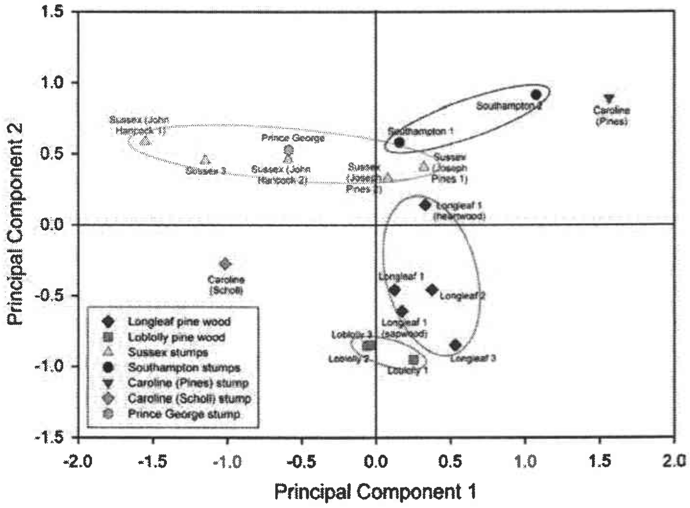
Highly weathered wood specimens were collected from stumps located in Caroline, Prince George, Southampton, and Sussex counties in Virginia. Wood shavings were analyzed by near infrared (NIR) spectroscopy with multivariate analysis, as described in Eberhardt and So (2005). Samples of longleaf and loblolly pine, obtained from recently harvested trees, were added to the NIR analysis to provide a reference point for these unknown stump samples. For the GC-MS analyses, wood shavings (1 g) from the specimens were steeped in methylene chloride (5 ml). GC-MS analyses of the resultant extracts were carried out on a Hewlett Packard 6890 gas chromatograph equipped with a Hewlett Packard 5973 mass selective detector and a HP-INNOWax column (0.25 mm ID × 60 m length × 25 µm film thickness). The temperature regimen of the column was programmed to hold for 1 min at 40 °C, increase to 80 °C at a rate of 16 °C min^{-1}, and then to 240 °C at a rate of 7 °C min^{-1}, with the final temperature being held for 10 minutes. The temperatures for the injector inlet and mass detector were maintained at 200 °C and 225 °C, respectively. Peaks were identified by spectral match with NIST 98 (NIST, Gaithersburg, MD) and in-house chemical libraries. Small wood blocks (*ca.* 1 cm^3) were also cut from the samples using a band saw. Specific gravity measurements were determined on weighed wood blocks by mercury displacement and also by careful measurement of block dimensions with a caliper. Extractives contents were determined by extracting wood blocks with methylene chloride for 3 days in a Soxhlet apparatus.

Results and Discussion

Taking into consideration signs of stump scarification and/or the occurrence of longleaf pine at the site (Southampton specimen, only), along with the reported ranges for each of the southern yellow pines, it appeared likely that the Southampton and Sussex county specimens were from longleaf pine trees. On the other hand, the Caroline (Scholl) specimen had a greater probability of being loblolly pine (*Pinus taeda* L.) because the collection site was outside the known range of longleaf pine and in a mixed hardwood/loblolly pine stand. Since wood structure cannot be used to differentiate between the southern yellow pines (Panshin and de Zeeuw 1980), our objective was to assess whether reported chemical and physical differences could be used for species identification.

Principal component analysis (PCA) was applied to the NIR spectra to observe any clustering and/or differences

Figure 1. Principal component analysis results from stump wood samples and longleaf and loblolly pine wood samples from recently harvested trees.



between the wood samples from the stumps and recently harvested trees. PCA was hindered by a lack of control samples, nevertheless, it was plausible that data gathered might be either indicative of longleaf pine or allow the elimination of other pine species. Several discrete groupings can be observed in the analysis of the PCA scores (Figure 1). The highly weathered stump samples clearly separate out from the recently harvested longleaf and loblolly pine samples. The samples from recently harvested trees further separate into loblolly and longleaf pines. As one would expect, the stump samples are closer to the longleaf heartwood sample than to the sapwood sample. Tentative groupings can be formed for the Sussex and Southampton samples. The Caroline (Scholl) sample appears closer to the recently harvested trees than the stumps, and if all the stump samples are assumed to be longleaf pine, the Caroline (Scholl) sample could possibly be another species such as loblolly pine.

Given their fragrant nature, the stump wood samples were also subjected to analysis by GC-MS to determine if significant amounts of monoterpenes remained despite many years of weathering. The ability to obtain seemingly representative monoterpene compositions suggested an opportunity to develop a chemotaxonomic approach to determine the stump taxa. Reported analyses of fresh oleoresin from most southern yellow pines (e.g., *P. palustris, P. taeda, P. echinata, P. elliottii*) have shown α-pinene to comprise 50-80% of the monoterpenes detected (Hodges et al. 1979, Strom et al. 2002). The second most abundant monoterpene, β-pinene, ranges from 20-40%. Along with the pinenes, much smaller amounts of camphene, myrcene, and limonene are also typically reported. Pond pine (*Pinus serotina* Michx.) is the exception among the southern yellow pines with limonene comprising as much as 90% of the detected monoterpenes (Mirov 1961). We hypothesized that comparisons of the monoterpene compositions with those from other stumps, in conjunction with available data for the oleoresin from recently harvested trees, might allow the stump species identification.

We found α-pinene to be the most abundant monoterpene in 4 of the 6 samples, comprising 40-50% of the volatiles detected (Table 1). In contrast to that for fresh oleoresin, the amounts of β-pinene in the stump wood samples were greatly diminished. Since β-pinene has a higher boiling point than α-pinene, the higher rate of loss of β-pinene was attributed to its lower stability rather than higher volatility. The second most abundant compound detected for these samples was the oxidized monoterpene, α-terpineol; significant amounts of other oxidized monoterpenes (e.g., camphor, fenchyl alcohol, borneol) were also observed. This result was not surprising since wood naval stores (i.e., that from old pine stumps) have been reported to contain high amounts (50-60%) of α-terpineol (Buchanan 1963). Given the similarity in the monoterpene compositions between samples taken from sites within (Southampton and Sussex counties) and outside (Caroline) the known range for longleaf pine, the similarity of the monoterpene compositions between the longleaf pine and loblolly pine oleoresin from live trees, and within-sample variability, it was not possible to identify the stumps as longleaf pine apart from the other southern pines. However, these data do suggest that none of the original trees were pond pine for which limonene is the predominant monoterpene. Limonene is a thermal isomerization product of α-pinene (Derfer and Traynor 1989, Drew et al. 1971) and thus it is unlikely that the high relative amounts of α-pinene detected could be derived

Table 1. Percentage compositions of monoterpenes and methylchavicol detected in stump wood samples.

Monoterpene	Caroline (Scholl)	Caroline (Pines)	Prince George	South-ampton	Sussex (John Han-cock)	Sussex (Joseph Pines)
	Stump Wood Samples					
α-pinene	47.37[a]	48.59	18.06	58.22	12.07	45.30
α-fenchene	0.80	0.42	3.14	0.58	5.60	0.74
camphene	3.59	0.24	5.46	3.10	7.58	2.99
β-pinene	1.55	2.40	nd	1.25	nd	2.75
myrcene	1.29	1.88	nd	0.03	nd	0.19
α-phellendrene	nd[b]	3.23	0.41	nd	nd	nd
α -terpinene	nd	1.26	1.33	nd	nd	nd
limonene	10.96	8.80	1.63	9.29	0.43	4.61
ß-phellendrene	nd	6.58	nd	nd	nd	0.31
p-cymene	0.74	0.11	47.97	0.28	19.14	1.40
terpinolene	1.26	2.23	1.89	1.68	nd	1.11
fenchone	0.36	nd	2.88	0.26	13.89	2.32
camphor	1.10	nd	6.58	0.82	19.95	4.36
fenchyl alcohol	2.83	2.78	1.69	1.92	0.15	0.89
terpinen-4-ol	1.62	0.56	1.97	0.93	11.22	3.64
methylchavicol	0.20	0.63	nd	2.55	0.52	6.89
α-terpineol	23.55	17.03	4.72	16.18	7.27	21.58
borneol	2.78	3.26	2.27	2.91	2.18	0.92

[a]percent peak area for identified compounds
[b]nd (not detected)

from a monoterpene composition predominated by limonene. In addition to the monoterpenes, methylchavicol (*p*-allylanisole) was detected in all but the Prince George sample. Its presence affords few clues to a specific pine species.

Analyses of the Prince George and Sussex (John Hancock) samples were particularly interesting since they showed an even greater degree of monoterpene oxidation. In these samples, the amounts of α-pinene and α-terpineol were significantly lower while higher amounts of *p*-cymene, fenchone, camphor, and terpinen-4-ol were present. At this juncture, it should be recognized again that very little data is available relating monoterpene compositions to age and species for very old southern yellow pine stumps. In one case, it has been suggested that the inherent acidity of wood promotes the conversion of α-pinene to cymene (Drew et al. 1971). Elevated temperatures have been shown to promote monoterpene oxidation (McGraw et al. 1999). Accordingly, it is speculated that these two trees (Prince George and Sussex (John Hancock)) were harvested much earlier than the others and/or were exposed to high temperatures during forest fires. In fact, burn scars on the Sussex (John Hancock) sample indicate the exposure to fires that one would expect in a longleaf pine ecosystem. Reported specific gravity values for the wood from the southern yellow pines show a lower value for loblolly pine as compared to

Table 2. Specific gravity and non-volatile extractives contents of stump wood samples.

Stump Wood Sample	Specific Gravity (gcm^{-3}) Before Extraction	Specific Gravity (gcm^{-3}) After Extraction	Non-Volatile Extractives (%)
Southampton	0.94 ± 0.08	0.56 ± 0.03	42.98
Caroline (Scholl)	0.70 ± 0.03	0.57 ± 0.02	10.44
Sussex (John Hancock)	0.76 ± 0.04	0.49 ± 0.03	35.29

longleaf pine (Wood Handbook 1974). Specific gravity values determined for the stump wood samples by the two different methods gave essentially the same result. All specific gravity values were significantly higher than those reported in the literature and reflect the very resinous nature of the samples (Table 2). These data illustrate that measurement of specific gravity, which can easily be carried out in the field, could be an alternative to extractions requiring solvents and laboratory facilities. Given the small difference in specific gravity for longleaf and loblolly pine woods, it is not surprising that the Southampton and Caroline (Scholl) samples have essentially the same specific gravity values after extraction. Since longleaf, and not loblolly pine, has an established history of use in naval stores production, highly resinous samples would seemingly have a greater likelihood of being longleaf pine. The high percentage of non-volatile extractives in the Southampton and Sussex (John Hancock) samples may reflect their use for naval stores production and provide a tantalizing clue that their identity may be longleaf pine.

Conclusions

Similarities in the monoterpene compositions for the fresh oleoresin of the southern yellow pines, and a lack of information about the volatilization and degradation of the monoterpenes in the natural environment, greatly limit our ability to assign the monoterpene compositions for our stump wood samples to specific pine species. However, pond pine was excluded since it differs from most of the other southern yellow pines with a monoterpene composition predominated by limonene. High extractive yields from resinous stumps can be readily estimated by specific gravity. A high extractive yield can be used to infer those southern yellow pine species used for naval stores production, specifically, longleaf and slash pines.

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